

University of Groningen

## Molecular motors with new topologies

Caroli, Giuseppe

**IMPORTANT NOTE:** You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*

2010

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Caroli, G. (2010). *Molecular motors with new topologies*. s.n.

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

# **Molecular motors with new topologies**

Giuseppe Caroli



**university of  
 groningen**

**faculty of mathematics  
and natural sciences**

The work described in this thesis was carried out at the Stratingh Institute for Chemistry, University of Groningen, The Netherlands.

The work described in this thesis was financially supported by the Ubbo Emmius scholarship.

On the cover: "*The rest of the plofkamer*", by G. Caroli.

The picture was taken with a Canon EOS 550D equipped with a Canon EFS 18-55mm lens (both kindly provided by E. Halza) [1/2 s, f/22.6, ISO 400, 18mm] and edited with appropriate software.

Printed by Ipskamp Drukkers, Enschede, The Netherlands.

ISBN: 978-90-367-4581-9 (printed version)

ISBN: 978-90-367-4582-6 (electronic version)

"Basic research is what I am doing when I don't know what I am doing."

*(Werner Von Braun)*



RIJKSUNIVERSITEIT GRONINGEN

# **Molecular motors with new topologies**

Proefschrift

ter verkrijging van het doctoraat in de  
Wiskunde en Natuurwetenschappen  
aan de Rijksuniversiteit Groningen  
op gezag van de  
Rector Magnificus, dr. F. Zwarts,  
in het openbaar te verdedigen op  
vrijdag 19 november 2010  
om 14:45 uur

door

**Giuseppe Caroli**

geboren op 11 februari 1977  
te Pompei, Italië

Promotor:

Prof. dr. B. L. Feringa

Beoordelingscommissie:

Prof. dr. A. Minnard

Prof. dr. A. Rowan

Prof. dr. A. Credi

ISBN: 978-90-367-4581-9 (printed version)

ISBN: 978-90-367-4582-6 (electronic version)

# *Table of contents*

## CHAPTER 1

INTRODUCTION TO MOLECULAR NANOTECHNOLOGY. MOLECULAR MOTORS: THEORETICAL ASPECTS, NATURAL AND SYNTHETIC EXAMPLES....1

<b>1.1 Key definitions</b> .....	2
<b>1.2 “There is plenty of room at the bottom” - The beginning of Nanotechnology</b> .....	2
1.2.1 Approaches to Nanotechnology .....	5
<b>1.3 Molecular machines: theory</b> .....	5
1.3.1 Nano objects do it different .....	5
1.3.2 The ‘power stroke’ model .....	6
1.3.3 The Brownian ratchet model.....	6
1.3.4 Power stroke vs. Brownian ratchet.....	7
<b>1.4 Molecular machines: examples from nature</b> .....	10
1.4.1 Myosin.....	10
1.4.2 Kinesin.....	11
1.4.3 Dynein .....	12
1.4.4 Flagellar motor.....	13
1.4.5 ATP synthase .....	14
<b>1.5 Molecular machines: synthetic examples</b> .....	16
1.5.1 Translational motors.....	16
1.5.2 Rotational motors .....	29
1.5.2.1 Molecular rotary motors in a more complex topology .....	39
1.5.2.2 Molecular rotors to come .....	44
<b>1.6 Conclusions and content of this thesis</b> .....	47

## CHAPTER 2

FIRST GENERATION 5-5 MEMBERED RING MOLECULAR MOTORS: FURTHER STUDIES AND DERIVATIZATION WITH LONG ALKYL CHAINS.....53

<b>2.1 Introduction</b> .....	54
2.1.1 First generation five-membered ring molecular motor derivatized with long alkyl chains .....	55
2.1.2 Calculations on the thermal isomerizations of motor <b>2.2</b> .....	57
2.1.3 New measurements of motor <b>2.2</b> .....	58
<b>2.2 A molecular motor derivatized with long alkyl chains</b> .....	58
2.2.1 Retrosynthetic analysis.....	59
2.2.2 Synthesis.....	59



2.2.3 $^1\text{H}$ -NMR measurements.....	61
2.2.4 UV/Vis measurements .....	64
2.2.5 CD measurements .....	67
2.2.6 Kinetic analysis .....	69
2.2.7 Conclusions.....	70
<b>2.3 <u>Five-five membered rings first generation molecular motor: a computational study</u></b> .....	71
2.3.1 Introduction.....	71
2.3.2 Results.....	72
<b>2.4 <u>New <math>^1\text{H}</math>-NMR study on the 5-5 membered ring motor 2.2</u></b> .....	80
2.4.1 $^1\text{H}$ -NMR: measurements.....	80
2.4.2 $^1\text{H}$ -NMR: calculations.....	83
2.4.3 CD calculations .....	87
<b>2.5 <u>Conclusions</u></b> .....	90
<b>2.6 <u>Experimental Section</u></b> .....	90
2.6.1 General remarks .....	90
2.6.2 Computational details .....	91

## CHAPTER 3

NEW TOPOLOGIES OF MOLECULAR MOTORS: MOTORS WITH LOOPS. A MOLECULAR SKIPPING ROPE AND A MOLECULAR STRAITJACKET. .... 99

<b>3.1 <u>Introduction</u></b> .....	100
<b>3.2 <u>Design and synthesis</u></b> .....	102
<b>3.3 <u>Study of the methyl ether motor</u></b> .....	115
3.3.1 $^1\text{H}$ -NMR measurements.....	115
<b>3.4 <u>Study of the large-looped motor</u></b> .....	118
3.4.1 Molecular modeling .....	118
3.4.2 $^1\text{H}$ -NMR measurements.....	119
3.4.3 UV/Vis measurements .....	124
3.4.4 Kinetic analysis .....	125
<b>3.5 <u>Study of the short-looped motor</u></b> .....	127
3.5.1 Crystallographic analysis and molecular modeling.....	128
3.5.2 $^1\text{H}$ -NMR measurements.....	134
3.5.2.1 <b>Conclusions</b> .....	138
3.5.3 UV/Vis measurements .....	138
3.5.4 CD measurements .....	140
<b>3.6 <u>Study of the hydrogenated short-looped motor</u></b> .....	142
3.6.1 Molecular modeling .....	143
3.6.2 $^1\text{H}$ -NMR measurements.....	144
3.6.3 UV/Vis measurements .....	146
3.6.4 Conclusions.....	147

<b>3.7 <u>Conclusions</u></b> .....	148
<b>3.8 <u>Experimental section</u></b> .....	149
3.8.1 General remarks .....	149
3.8.2 Computational details .....	149

## CHAPTER 4

DIMERS OF MOLECULAR MOTORS IN A MACROCYCLIC AND LINEAR TOPOLOGY .....	175
<b>4.1 <u>Introduction</u></b> .....	176
<b>4.2 <u>Synthesis</u></b> .....	176
4.2.1 Retrosynthesis .....	177
4.2.2 Synthesis .....	179
<b>4.3 <u>Molecular modeling</u></b> .....	185
<b>4.4 <u><sup>1</sup>H-NMR measurements</u></b> .....	187
4.4.1 <sup>1</sup> H-NMR measurements on the monomer .....	187
4.4.2 <sup>1</sup> H-NMR measurements of the linear dimer .....	190
4.4.3 <sup>1</sup> H-NMR measurements of the cyclic dimer .....	193
<b>4.5 <u>Conclusions</u></b> .....	196
<b>4.6 <u>Experimental section</u></b> .....	198
4.6.1 General remarks .....	198
4.6.2 Computational details .....	198

## CHAPTER 5

INCREASING THE STABILITY OF FUNCTIONALIZED MOLECULAR MOTORS. A NEW SHORT LOOPED MOLECULAR MOTOR, A MOLECULAR WALKER, AND A FUNCTIONALIZED MOLECULAR MOTOR FOR LIQUID CRYSTALS. ....	207
<b>5.1 <u>Introduction</u></b> .....	208
<b>5.2 <u>Design and synthesis of the scaffold</u></b> .....	209
<b>5.3 <u>The molecular walker</u></b> .....	213
5.3.1 Introduction .....	213
5.3.2 Synthesis .....	215
5.3.3 <sup>1</sup> H-NMR measurements .....	216
5.3.4 UV/Vis measurements and kinetic study .....	220
<b>5.4 <u>The LC dopant motor</u></b> .....	223
5.4.1 Introduction .....	223
5.4.2 Synthesis .....	225
5.4.3 <sup>1</sup> H-NMR measurements .....	226
5.4.4 UV/Vis measurements and kinetic study .....	230
<b>5.5 <u>A new looped motor</u></b> .....	234

5.5.1 Introduction.....	234
5.5.2 Synthesis .....	234
5.5.3 UV/Vis measurements .....	235
<b>5.6 Conclusions</b> .....	238
<b>5.7 Experimental section</b> .....	239
5.7.1 General remarks .....	239
5.7.2 Computational details .....	239

## CHAPTER 6

### MOLECULAR MOTORS WITH AROMATIC GROUPS AT THE STEREOGENIC CENTERS .....

<b>6.1 Introduction</b> .....	252
<b>6.2 Aryl motor</b> .....	255
6.2.1 Retrosynthetic analysis .....	255
6.2.2 Synthesis .....	255
6.2.3 Molecular modeling .....	256
6.2.4 <sup>1</sup> H-NMR measurements.....	259
6.2.5 UV/Vis measurements .....	266
6.2.6 Kinetic analysis .....	268
<b>6.3 Benzyl motor</b> .....	270
6.3.1 Retrosynthetic analysis .....	270
6.3.2 Synthesis .....	270
6.3.3 Molecular modeling .....	272
6.3.4 <sup>1</sup> H-NMR measurements.....	275
6.3.5 UV/Vis measurements .....	278
6.3.6 Kinetic study.....	281
<b>6.4 Biphenyl motor</b> .....	282
6.4.1 Retrosynthetic analysis .....	282
6.4.2 Synthesis .....	283
6.4.3 Molecular modeling .....	283
6.4.4 <sup>1</sup> H-NMR measurements.....	287
6.4.5 UV/Vis measurements .....	290
6.4.6 Kinetic study.....	292
<b>6.5 <i>p</i>-Phenyl-benzyl motor</b> .....	294
6.5.1 Retrosynthetic analysis .....	294
6.5.2 Synthesis .....	295
6.5.3 Molecular modeling .....	295
6.5.4 <sup>1</sup> H-NMR measurements.....	299
6.5.5 UV/Vis measurements .....	302
6.5.6 Kinetic study.....	305
<b>6.6 Conclusions and discussions</b> .....	306

<b>6.7 Experimental section</b> .....	309
6.7.1 General remarks.....	309
6.7.2 Computational details.....	309

## CHAPTER 7

### INTRAMOLECULAR ROTAXANE FORMATION USING A ROTARY MOLECULAR MOTOR: A MOLECULAR REEL.....

<b>7.1 Introduction</b> .....	326
<b>7.2 Concept, design and modeling</b> .....	327
7.2.1 Concept.....	327
7.2.2 Molecular design and envisioned working mechanism.....	329
7.2.3 Molecular modeling .....	330
7.2.3.1 Analysis of the winding process and of the length of the threads .....	331
7.2.3.2 Conclusions on the rotaxane formation process.....	339
<b>7.3 Retrosynthetic analysis and synthesis</b> .....	339
7.3.1 Final definition of the targets.....	339
7.3.2 Retrosynthetic analysis and synthesis of the model system .....	340
7.3.2.1 Retrosynthetic analysis .....	340
7.3.2.2 Synthesis .....	343
7.3.3 Synthesis of the stopper-thread moiety .....	351
7.3.4 Synthesis of the molecular reel.....	353
7.3.5 Conclusion.....	357
<b>7.4 <sup>1</sup>H-NMR measurements</b> .....	357
7.4.1 <sup>1</sup> H-NMR measurements of the model system .....	357
7.4.1.1 Conclusions on the spectroscopic study of the model system .....	362
7.4.2 <sup>1</sup> H-NMR measurements of the molecular reel .....	363
7.4.2.1 Discussion on the isomerization study of the molecular reel.....	369
<b>7.5 Conclusions</b> .....	372
<b>7.6 Experimental section</b> .....	374
7.6.1 General remarks.....	374
7.6.2 Computational details.....	374

Samenvatting .....	396
--------------------	-----

Summary.....	397
--------------	-----

Riassunto .....	402
-----------------	-----

Acknowledgments .....	408
-----------------------	-----

